Studies on the Flame Spectrochemical Analysis. II : Determination of Microamount of Calcium and Magnesium

著者	IKEDA Shigero
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	7
page range	575-582
year	1955
URL	http://hdl.handle.net/10097/26740

Studies on the Flame Spectrochemical Analysis. II
Determination of Microamount of Calcium and Magnesium*

Shigerô IKEDA
The Research Institute for Iron, Steel and Other Metals
(Received September 12, 1955)

Synopsis

Various alcohols were adopted as solvents to intensify the excitation of flame emission of calcium and magnesium. Methyl alcohol was found to be the most effective solvent to rise the sensitivity of the emission intensity of these two elements. Also the influences of acids and some diverse elements were studied and the various conditions of applying this solvent effect to the microdetermination of calcium and magnesium were investigated.

I. Introduction

The flame spectrographic determination of calcium was first carried out by Lnndegårdh[1]. Recently, calcium in plant or water was determined using a flame spectrophotometer, while the flame spectrophotometric determination of magnesium had never generally been applied in the routine analysis. The applicable ranges of the flame spectrophotometric analysis differ with the sensitivity of the instrument itself used, but, generally, the flame sensitivity for the determination of calcium and magnesium is lower than that for sodium or potassium. In this report, the effects of various alcohols on the flame emission of calcium or magnesium were studied and then the suitable conditions for the determination of these elements in dilute concentration was established.

II. Reagent and instrument

The standard solution of calcium (lmg/ml) was made by dissolving kahlbaum analytical reagent grade calcium carbonate with hydrochloric acid and was kept as 0.01N hydrochloric acid solution. The standard solution of magnesium was also prepared as above by using magnesium oxide and the concentration of it was kept to lmg/ml in 0.01N hydrochloric acid solution and diluted when it was used.

Alcohols and water used in the experiment was all redistilled. The flame spectrophotometric measurement was made by Beckman model DU spectrophotometer with 9200 flame attachment. The sample was emitted by hydrogen-oxygen flame and the wave lengths selected for the measurement were 554 mμ for calcium and 371 mμ for magnesium.

---

* The report of the Research Institute for Iron, Steel and Other Metals. Read at 2th Annual Meeting of the Japan Soc. for Anal. Chem. Oct., 1953.

(1) H. Lundegårdh, *Die quantitative Spektralanalyse der Elemente*, 2 Teil (1934)

III. Calcium

1. Gas pressure

Oxygen pressure was adjusted to 25 lb/in^2 and the change of the emission intensity of calcium solution of 0.5γ/ml in concentration was observed at various hydrogen with 0.3 mm slit width. Next, hydrogen pressure was kept at 3lb/in^2 and the emission intensity of calcium was measured at various oxygen pressure. These results were shown in Fig. 1. The emission was most intense with hydrogen pressure at 2.8 $\sim$3.5 lb/in^2 and oxygen pressure at 25 lb/in^2. From this result, in the experiment for calcium investigation, hydrogen pressure was kept at 3.0lb/in^2 and oxygen at 25lb/in^2.

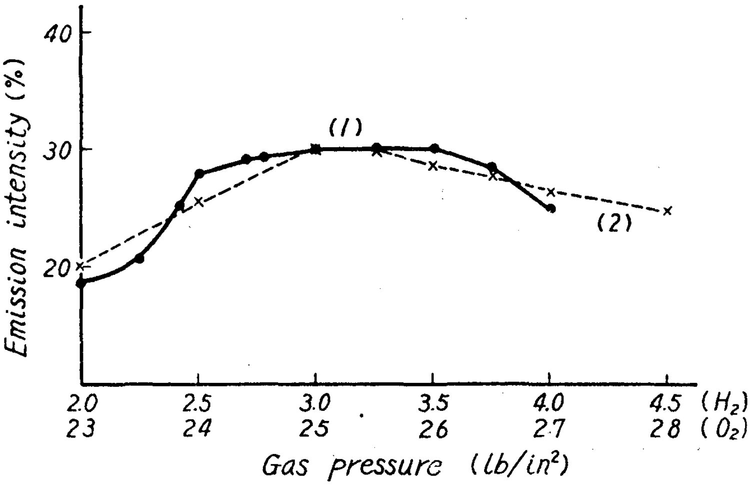

Fig. 1. Relation between gas pressures and flame intensity.
(1) Relation of intensity with H_2 pressure at O_2 25 lb/in^2.
(2) Relation of intensity with O_2 pressure at H_2 3 lb/in^2.

2. The change of emission of calcium in the various solvents

When the emission intensity of calcium with various concentrations in aqueous solution was measured at 0.5 mm slit width, it was found,as shown in Fig. 2. curve(1), that although the determinable limit of calcium in aqueous solution might be said to be 0.1γ/ml, but its calibration curve was slow. Bahrnes[(2)] reported on the successful results of the flame emission of alkali metals using organic solvents. In the present experiments, methyl alcohol, ethyl alcohol or isopropyl alcohol was added to the calcium solution, and the emission intensity of the solution was measured. In Fig 2, the calibration

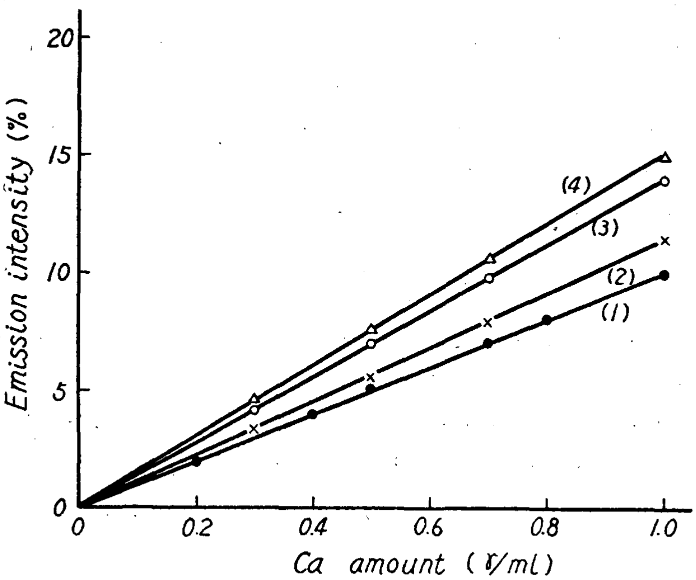

Fig. 2. Calibration curve of calcium in various solvents.
(1) Aqueous solution.
(2) Isopropyl alcohol solution (50%).
(3) Ethyl alcohol solution (50%).
(4) Methyl alcohol solution (50%).

(2) R B. Bahrnes, J. W. Bery and D. G. Chappel, Ind. Eng. Chem., Anal. Ed. **18** (1946), 19.

curves of calcium to its emission intensity with 50 per cent alcoholic solutions were graphed. The emission became intenser in the order of methyl alcoholic, ethyl alcoholic and isopropyl alcoholic solution. The experimental technique was carried out as follows: the emission intensity of calcium solution of 1 γ/ml was adjusted to 30 per cent of transmittancy scale reading, and the intensities of calcium solution in various concentrations and background in each solvent were measured, and the intensity of calcium was obtained by subtracting the background intensity from the calcium solution intensity.

In Table 1, the intensity of calcium of 0.5 γ/ml and 1 γ/ml in each 50 per cent

Table 1. Calcium emission intensity in various solvents

Solvent	Ca 1 γ/ml		Ca 0.5 γ/ml	
	Intensity measured (%)	Standard deviation (%)	Intensity measured (%)	Standard deviation (%)
aqueous solution	9.8	± 0.14	4.9	± 0.12
methyl alcohol	15.8	± 0.17	8.2	± 0.15
ethyl alcohol	14.8	± 0.17	7.5	± 0.16
isopropyl alcohol	12.2	± 0.16	6.0	± 0.15

i) Intensity was mean value of five measurements.
ii) Alcohol concentration was 50% in each solution.
iii) All solution were acidified with hydrochloric acid to 0.1N.

alcoholic solution and aqueous solution, and the ratios of their intensities in alcoholic solution to those in aqueous solution were given. Then the sensitivity of calcium measurements would become remarkably higher in alcoholic solution than in aqueous solution with the order of methyl alcohol, ethyl alcohol and isopropyl alcohol. The intensity in 50 per cent methyl alcoholic solution was about 1.7 times strong as that in aqueous solution. Next, the relations between the concentration of alcohol and the intensity of calcium was researched with methyl alchol and isopropyl alcohol and the results are shown in Fig. 3. As shown in Fig. 3, the concentration

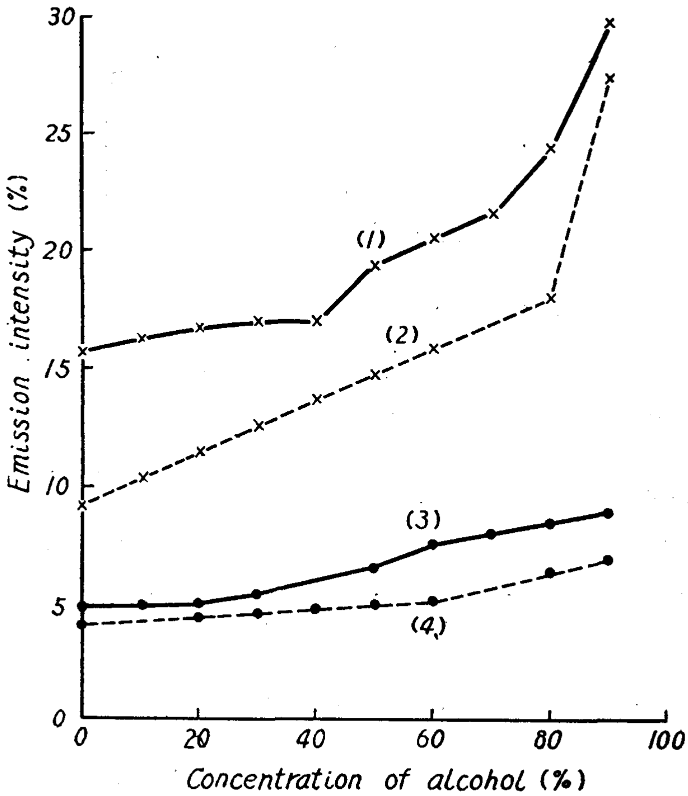

Fig. 3. Relation between alcohol concentration and emission intensity of calcium.
(1) Isopropyl alcohol Ca 1 γ/ml.
(2) Methyl alcohol Ca 0.5 γ/ml.
(3) Isopropyl alcohol Ca O.
(4) Methyl alcohol Ca O.
Slit width 0.5 mm.

change of methyl alcohol gives more influences to the emission intensity than that of isopropyl alcohol gives. In each case, the intensity of cacilum increased with the increase in alcohol concentrations. Background, however, increased only slightly in proportion to the concentration of alcohol and its change was very small, compared with that of calcium solution. In the dilute concentration of isopropyl alcohol, the increase in the intensity was comparatively small, but over 40 per cent, the influence of the alcohol concentration became severe. These results led the conclusion that for the determination of calcium using alcoholic solution, the concentration of alcohol must be kept constant.

3. Concentration of acid

It was seen that the enlargement of the determinable range of the microamount of calcium was pessible by the flame spectrophotometric method and by using some alcohols as solvent. Next, the investigation was carried out about the influences of the change of the acid concentration added in the sample solution on the emission intensity of calcium, and the results obtained are shown in Table 2. Hydrochloric acid did not affect till the concentration became 1.5N in the solution,

Table 2. Influences of acid on calcium emission

Concentration (N)	H Cl	HNO_3	Concentration (N)	H_2SO_4
0.1	8.2	8.2	0.1	8.1
0.5	8.2	8.1	0.2	7.8
1	8.0	7.9	0.3	7.3
1.5	8.0	7.5	0.5	7.3
2	7.8	7.5	1.0	7.3
3	7.6	7.5	2.0	7.3
5	7.6	7.5	3.0	7.1

i) Intensity were mean values of five measurement of 0.5 γ/ml of calcium in 50% methyl alcohol solution.
ii) Permissible deviation was $8.2 \pm 0.3\%$.

but over 1.5N it caused the decrease in intensity, and with the higher concentration 3N the intensity of calcium became stable again. Nitric acid effected already with 0.5N but the emission was stable in the concentration over 0.5N. Sulfuric acid decreased greatly the calcium intensity and gave the stable emission in the range of 1N to 5N. In these experiments, 50 per cent methyl alcoholic solution containing 0.5 γ/ml of calcium was used. When isopropyl alcohol was used as solvent, the result was also the same as above, except that the decreases of the intensity causing to the increase of acids concentration were compratively small.

4. Diverse elements

The influences of some diverse elements on the flame emission of calciun in 50 per cent methyl alcoholic solution were researched. In Table 3, the permissible amounts of diverse elements for the determination of calcium by this method was listed. a little quantities of phosphorous prevented the calcium determination, but its permissible limit of concentration to present without interference was rather higher than that when aqueous solution was used.

Table 3. Influences of diverse elements on calcium emission and permissible amonnt of elements for the calcium determination (γ/ml)

element	Ca (1γ/ml)	Ca (0.5γ/ml)	Ca (0.1γ/ml)	Intensity change
Al	0.5	0.3	0.1	−
Ba	10	10	5	+
Cu	10	6	3	−
Fe	10	8	1	−
Mg	10	10	3	+
Na	6	6	3	−
K	8	8	5	−
PO_4^{3-}	0.7	0.3	0.1	−

i) 50% methyl alcohol solution
ii) 0.1 N HCl.
iii) Permissible error ± 3%.

5. Conclusion

From these results obtained above it was concluded that the addition of alcohol in the sample solution of calcium made possible to increase the sensitivity of calcium determination in flame spectrophotometric analysis. The emission intensity of calcium had the linear relation with the concentration of calcium in the solution with a definite concentration of alcohol. The experiments for the investigation of the influences of acids or some diverse elements on the calcium flame emission in alcoholic solution using 0.5 γ/ml of calcium gave almost the same result as in aqueous solution. So the usage of alcohol was very effective for the microdetermination of calcium with precision in aqueous solution.

IV. Studies on the magnesium emission

1. Gas pressure and wave length for magnesium emission

The suitable hydrogen and oxygen pressures for the magnesium emission was investigated with the aqueous solution of magnesium (0.5 γ/ml). The flame emission of magnesium was generally measured with the band head at 371~383 mμ or the line spectrum at 285 mμ. When the measurement was carried out using Beckman model DU spectrophotometer, the emission was most intense at 371 mμ. So the wave length for the measurement of magnesium emission was selected to 371 mμ. By keeping the oxygen pressure 25 lb/in^2, hydrogen pressure was changed and the emission intensity was observed. The intensity was increased gradually with the increase of hydrogen pressure but its increase became very slight when hydrogen pressure was over 3.7 lb/in^2. When the suitable oxygen pressue was researched with 4 lb/in^2 of hydrogen pressure, the emission was most intense and stable at 28~30 lb/in^2 of oxygen. From these result, the flame in following experiments was emitted using 4 lb/in^2 of hydrogen pressure 30 lb/in^2 with the slit width of 0.5 mm.

2. The emission of magnesium in various solvents

Magnesium in aqueous, 50 per cent methyl alcohol, 50 per cent ethyl alcohol or 50 per cent isopropyl alcohol with the concentration of 5 γ/ml was emitted and the

Table 4. magnesium flame emission in various solnents

Solvent	Intensity measured (%)	Standard deviation (%)
aqueous solution	4.3	± 0.09
50% methyl alcohol solution	9.5	± 0.13
50% ethyl alcohol solution	8.8	± 0.09
50% isopropyl alcohol solution	8.6	± 0.10

Mg 5γ/ml, HCl 0.1N.

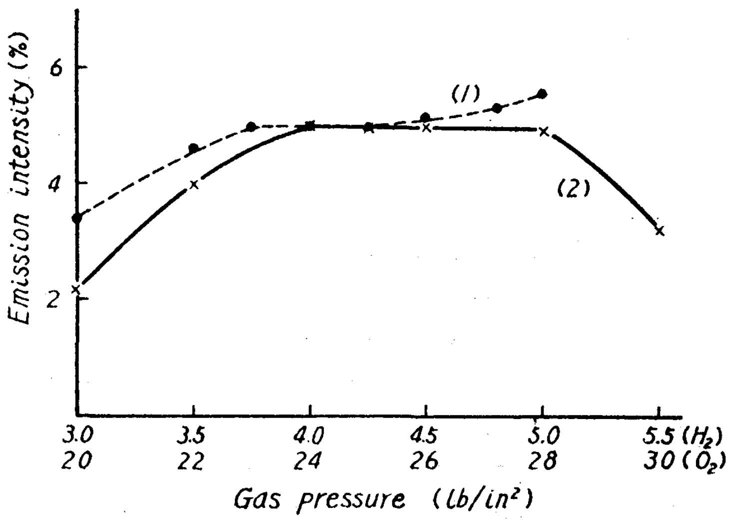

Fig. 4. Relation between magnesium emission and gas pressures.
(1) Relation between intensity and H_2 pressure at O_2 25 lb/in^2.
(2) Relation between intensity and O_2 pressure at H_2 4 lb/in^2.
Mg 5 γ/ml.
Slit width 0.5 mm, Wavelength 371 mμ.

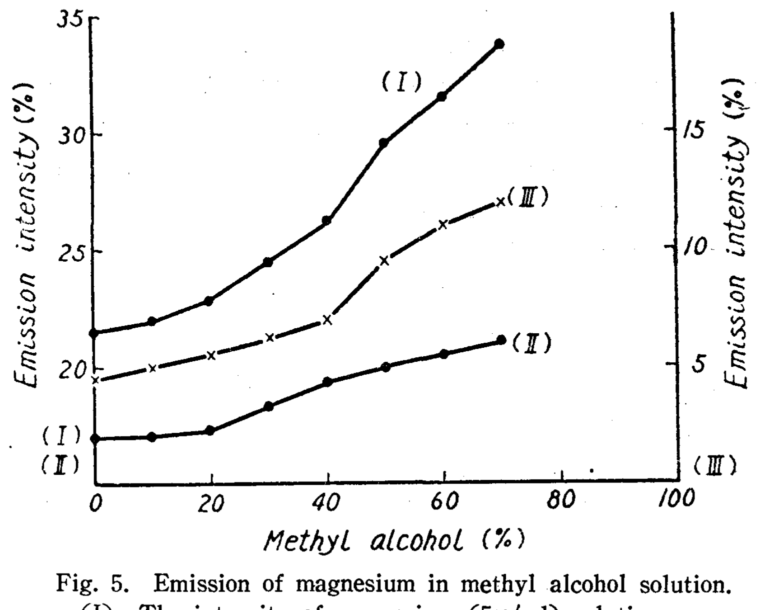

Fig. 5. Emission of magnesium in methyl alcohol solution.
(I) The intensity of magnesium (5γ/ml) solution.
(II) Background.
(III) The true intensity of magnesium (5 γ/ml).

intensity measured wre shown in Table 4. In Table 4, it was also listed the intensity ratio of magnesium in each alcoholic solution to the one in aqueous solution. From the result, it was found that alcohols were effective to intensify the magnesium flame emission. The most suitable gas pressure in these cases was the same as in aqueous solution and the standard deviation of each measurment was almost agreed in all three alcoholic solvents. So the permissible ranges of experimental error in the measurement of magnesium flame emission in the investigation could be made to 3 per cent. To research the relation between the emission intensity and the cocentration of alcohol in the solution, experiment was made with magesium solution in various concentration of methyl alcohol.

As shown in Fig. 5, the intensity increased remarkably by increasing the concentartion of methyl alcohol. From this result, for the determination of magnesium using alcohol as solvent in flame spectrophotometric method, the concentration of alcohol must be kept at a definite concentration. (I) In Fig. 5 shows the emission intencity of the alcoholic magnesium solution, (II) was background, and (III) shows the magnesium intensity obtaind by subtracting (II) from (I). Next, the calibration curve of magnesium was obtained by using aqueous solution and 50 per cent methyl alcohol solution and was shown in Fig. 6. The sensitivity of magnesium emission in the methyl alcoholic solution was twice as high as that in aqueous solution.

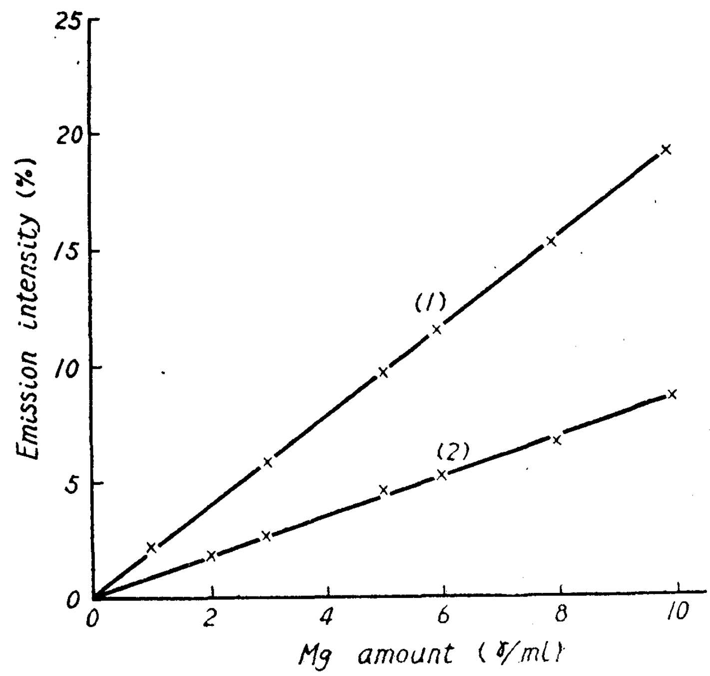

Fig. 6. Calibration curve for magnesium.
(1) 50% methyl alcohol solution.
(2) Aqueous solution.
Slit width 0.5 mm.

3. The influences of acids and diverse elements

The influences of some acid on the emissiom intensity of magnesium in methyl alcoholic solution (50 per cent) were investigated and the results are shown in Table 5. The permissible concentrations of acids for the determination of magnesium were as follows, hydrochloric acid was till 3N; nitric acid was till 1.5N and sulfuric acid was till 0.5N. Over these concentrations, magnesium emission decreased gradually. Next, various diverse elements were added in the 50 per cent methyl alcoholic solution of magnesium, and the influences of these

Table 5. Influences of acd on the magnesium emission in alcohol solution

Concentration (N)	H Cl	HNO_3	Concentration (N)	H_2SO_4
0.1	9.5	9.4	0.1	9.3
0.5	9.4	9.1	0.2	9.1
1.0	9.5	8.9	0.3	8 6
1.5	9.4	8.9	0.5	8.2
2.0	9.4	8.9	1.0	8.2
3.0	9.4	8.8	2.0	8.2
4.0	9.1	8.8	3.0	8.0

i) Table 5 shows the mean value of fine measurements of magnesium intensity (5 γ/ml) in 50% methyl alcohol.
ii) Permissible deviation was 9.5±0.3%.

elements on the flame emission of magnesium were researched and the permissible amounts for the microdetermination of magnesium with this condition were listed in Table 6. The permissible error was controlled to 3 per cent of the estimated results obtained with the solution containing magnesium only.

Table 6. Imfluences of diverse elements on the magnesium emission and permissibe amounts of them for magnesium determination. (γ/ml)

element	Mg (10γ/ml)	Mg (5γ/ml)	Mg (1γ/ml)	Intensity change
Al	10	10	3	−
Ba	30	15	10	+
Ca	10	5	5	+
Cu	4	4	3	−
Na	50	30	10	−
Fe	10	5	3	+
Mn	10	10	5	−
P	9	3	3	−
K	20	15	10	−

50% methyl alcohol solution, 0.1N HCl.
Permissible deviation ±3%.

4. Conclution

It was concluded from above results that, as resulted in calcium flame emission, the adoption of alcohol as solvent for the excitation of flame emissiom of magnesium was very successful, and the sensitivity of the intensity of the emission of magnesium in alcoholic solution would increase remarkably. So alcohol would be very useful for the microdetermination of magnesium. The acid concentration and the amounts of diverse elements permissible to present for the microdetermination of magnesium were either the same as or comparatively larger than that in aqueous solution.

Summary

(1) The utilization of alcoholic solution for the intensification of the flame emission of calcium and magnesium were effective.

(2) For the microdetermination of calcium or magnesium flame spectrophotometrically using these method, the concentration of alcohol must be kept in a definite one.

(3) The permissible concentrations of diverse elements for the determination of calcium or magnesium with alcoholic solution were also investigated and determined.

(4) By using alcoholic solution, 0.1γ/ml of calcium and 1γ/ml magnesium, could be determined with appreciably higher sensitivity than in aqueous solution.

Acknowledgement

The author wishes to express his hearty thanks to prof. H. Gotô for his helpful suggestion in the course of the present work.